Charge stock $C_7H_{15} \cdot C_{15}H_{30} \cdot C_7H_{15}$

                           Heavy gas oil

↓

Cracked stock $C_7H_{16} + C_{14}H_{28}{:}CH_2 + C_6H_{12}{:}CH_2$

                       Gasoline +   Recycle   +   Gasoline

                                     stock   (antiknock)

↓

More cracking $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18} + C_6H_{12}{:}CH_2)$

                       Gas   Gasoline

                                           $+ CH_2{:}CH \cdot CH{:}CH \cdot CH_3 - C_2H_4$

                                                     Gum-forming materials   Gas

↓

Polymerization $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18}) + C_{12}H_{22} + C_2H_4$

                       Gas   Tar or   Gas

                                                          recycle

All cracking reactions are endothermic and the energy involved is usually high. The reactions are sufficiently complicated to make accurate calculation of reaction heats difficult to impossible.
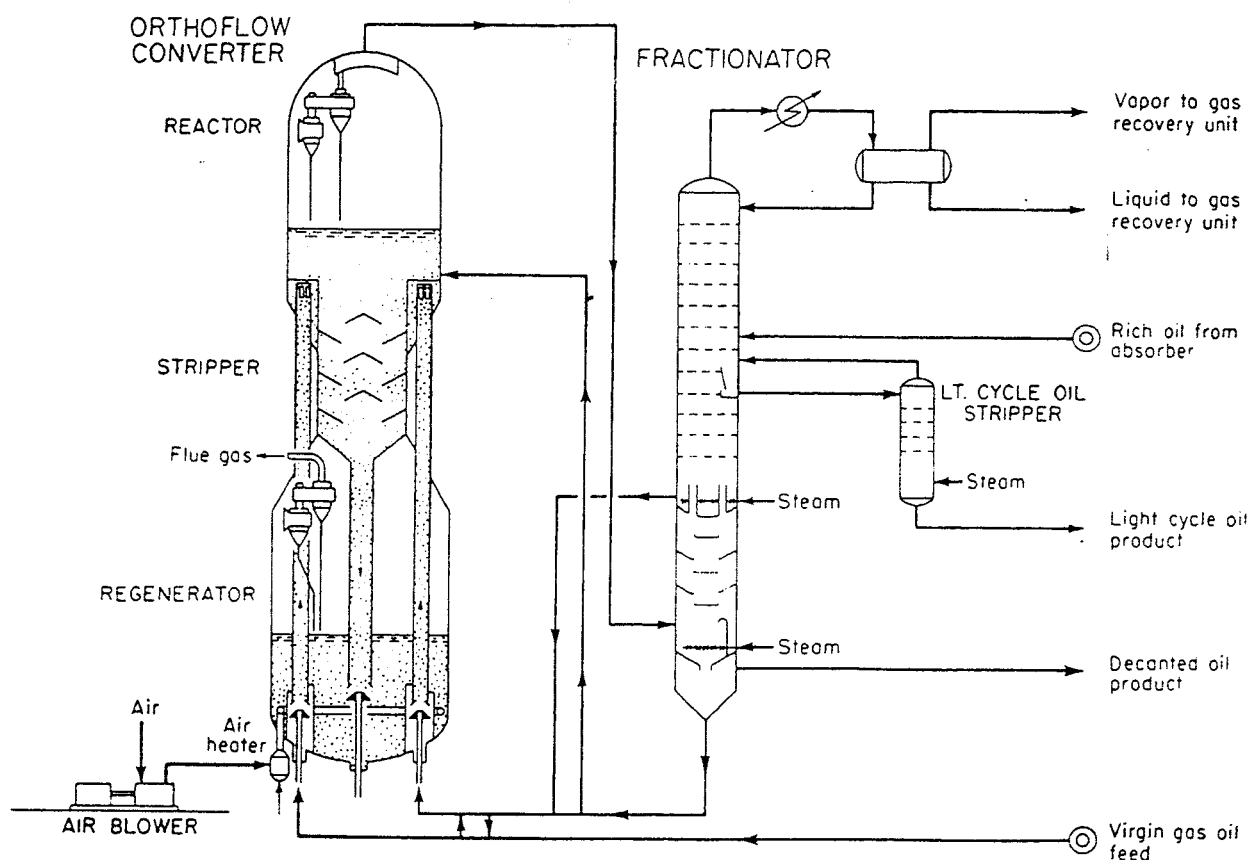
Cracking conserves fuel because it makes possible efficient use of virtually all the crude Gas oil was the original cracking stock. Present techniques make possible cracking of refinery naphthas and even of quite heavy stocks and reduced crude Essentially all present-day cracking is done in the presence of catalysts.

Catalytic cracking was first brought about by using fixed beds of catalyst. Such beds can function for only a few minutes before carbon deposition reduces or stops catalytic activity The bed must then be regenerated by burning the carbon off under carefully controlled conditions to avoid sintering of the catalyst and recover the valuable heat of its combustion Such units proved to be cumbersome and were soon replaced by several variants. First the catalyst was moved mechanically; later the fluid catalytic process took over. Engineers noted that with proper agitation, a finely divided suspension of solid in gas would flow like a liquid and could be handled with liquid pumps and exchange heat in double-pipe exchangers without settling. Because gas is light and the solid is heavy, the mixture tends to possess the properties of the solid, so the high specific heat makes temperature control remarkably precise Utilizing these principles enabled catalyst-vapor contact to be handled very well, temperature control to be greatly improved, and by moving the catalyst about as a fluid, it no longer was necessary to confine it to a bed-in-place. Cracking and regeneration took place in two units and the solids were separated from the vapors and flue gases by using cyclone separators. All cycles are continuous (Figs. 37.9 and 37.10).

The M. W. Kellogg Orthoflow and the newer Ultra-Orthoflow fluid cracking units[2] are typical of units carrying out reaction, catalyst stripping, regeneration, and catalyst circulation in a single converter (Figs. 37.9 and 37.10) The reactor is mounted above the regenerator and the catalyst stripping section is located in-between, so the stripper supports the reactor. The Orthoflow design provides straight-line flow of the catalyst between the converter compartments, virtually eliminating the erosion normally encountered in pipe bends Within the converter, the powdered synthetic catalyst is maintained in a fluidized bed by controlled

[1]Nelson, op. cit.

[2]*Hydrocarbon Process.* **58** (9) 131 (1979); 61 (9) 101 (1982).

ORTHOFLOW CONVERTER
REACTOR
STRIPPER
Flue gas
REGENERATOR
Air
Air heater
AIR BLOWER

FRACTIONATOR
Vapor to gas recovery unit
Liquid to gas recovery unit
Rich oil from absorber
LT. CYCLE OIL STRIPPER
Steam
Light cycle oil product
Steam
Decanted oil product
Steam
Virgin gas oil feed

Operating conditions can be described as follows:

	USUAL RANGES	TYPICAL CONDITIONS
Reaction temperature C°	475–550	496
Reaction pressure, kPa	170–310	163
Regenerator temperature, C°	675–760	621
Regenerator pressure, kPa	204–340	211
Catalyst/oil ratio	6–20	6.2
Space velocity, wt/wt-h	1.0–16.0	2.4

Yields from gasoline cracking can be varied within limits to suit a refiner's special local conditions. Typical yields from a Kellogg Orthoflow unit operating at a comparatively high conversion are:

Charge density	0.893	C_4 + gasoline, vol %	67.4
Throughput ratio	1.95	Light cycle oil, vol %	21.0
Conversion, vol %	76.0	Fractionator bottoms, vol %	3.0
C_2 and lighter, wt %	4.0	Coke, wt %	10.0
C_3, vol %	9.7		

Typical requirements,° unit per cubic meter of fresh feed:

Electricity, MJ	136	Water, boiler feed, m^3	0.286
Steam (generated), kg	(14.9)	Catalyst consumption, kg	0.09–0.18
Water, cooling (22° rise), m^3	7.55		

*Excludes recovery plant. Using electric drive on the air blower. There is a net production of steam. Also 39 MJ of heat is available for use in the recovery plant.

Fig. 37.9. Orthoflow catalytic cracking converter and adjuncts. Stippled areas represent fresh or regenerated catalyst. (M. W. Kellogg Co.)
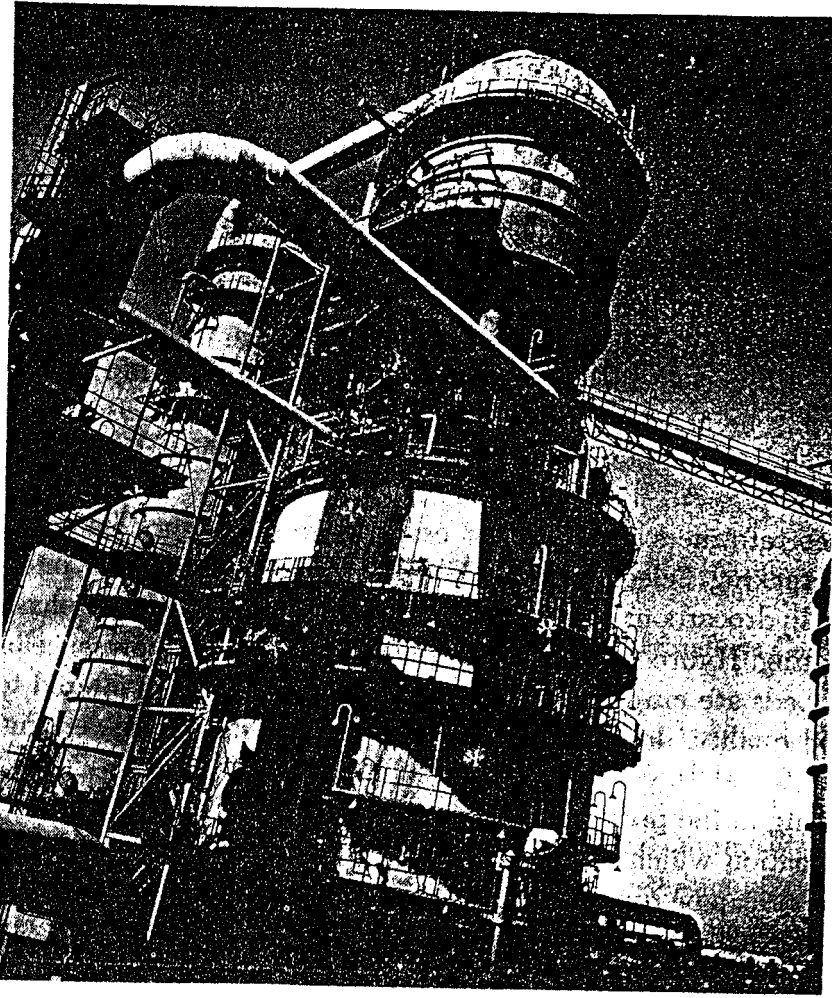
Fig. 37.10. Orthoflow catalytic cracker. *(M. W. Kellogg Co.)*

ing vapors. Circulation is maintained by having different concentrations in the catalyst circulation lines.

During operation, the hot catalyst from the regenerator enters the feed-regenerated catalyst risers through plug valves. Feed and dispersion streams are fed simultaneously through the hollow stem of the valves and mix with the catalyst. Heat from the regulated amount of hot catalyst vaporizes the oil and raises it to the required reaction temperature. As the oil and catalyst pass up the risers, the cracking reaction takes place. The risers terminate in the reactor, where additional cracking takes place, either in a dense bed or a disperse phase. The cracked products, steam, and inerts enter a disengaging space, from which the catalyst falls back into the bed. Reactor effluent passes upward through cyclones for separation of the catalyst from reactor overhead vapors. Spent catalyst from the cracking reaction leaves the reactor and passes through the stripper, where it is steam-stripped to remove cracked products and cycle oil trapped by the down-flowing catalyst. The stripper catalyst then falls, in a dense phase, down the spent-catalyst standpipes, through plug valves, and into the regenerator bed. Here coke laid down on the catalyst during reaction is burned off, using air. Combustion flue gas passes upward from the fluid bed through a disengaging zone and then through several stages of cyclones (usually two to three stages). The flue gas may be vented to the atmosphere or sent to CO boilers (where the CO contained in the flue gas is burned) for the generation of high-pressure steam.

Since the reactor effluent is a complex mixture of inerts, gas, butanes, gasoline, and cycle-oil stocks, it must be separated into the desired product streams. Reactor overhead vapors are separated in the catalytic fractionator. The vapors leaving the catalytic fractionator overhead

reflux drum contain valuable gasoline components, and the raw unstabilized (i.e., high vapor pressure) gasoline contains undesirable light hydrocarbons. The recovery, separation, and purification of these light ends and gasoline are accomplished in a gas-recovery plant which utilizes gas compression and recovery equipment in an absorption-and-fractionation system.

A valuable heating-oil product called light cycle oil is condensed in the section immediately above the heavy cycle-oil section of the tower. The light cycle oil is generally drawn from the tower as a side stream, stripped with steam, and sent to storage A rich oil stream is returned to the catalytic fractionation from the gas plant, where it has served as a sponge-oil medium to recover valuable hydrocarbons which otherwise would be lost to fuel gas.

This *fluid catalytic process* contributes a valuable principle to the chemical industry. The use of a large amount of turbulent solid capable of absorbing much heat in the reaction mass greatly reduces temperature variations and hot spots. If no catalytic action is desired, an inert, powdered solid may be used.

A wide variety of bed-in-place reformers and fluid-bed crackers go under such names as Isocracking, Ultracracking, Unicracking, Selectoforming, Ultracat, etc. The increasing interest in products from the heavier hydrocarbons at the "bottom of the barrel" places emphasis on hydrocracking and hydrotreating. Hydrocracking[39] is strong processing in the presence of hydrogen. Both fixed and fluid beds are employed. Light and heavy gas oils are altered to distillable light products of good quality, desulfured, demetallized, and stabilized. See Fig. 37.11.

Hydrotreating is mild processing in the presence of hydrogen, and desulfurizes, improves color, reduces metallic contamination which is destructive to cracking catalysts, improves storage stability, saturates olefins, or can be run selectively to saturate only diolefins. Improvements in specialty products are particularly marked.

REFORMING. Reforming means just what the name implies—forming new molecules of a size similar to the original ones. Because the octanes of straight run gasolines, naphthas, and

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[39]Menzies, Silva, and Denis, Hydrocracking without Catalysis Upgrades Heavy Oil, *Chem Eng.* **88** (4) 46 (1981); Details of Dynacracking Process Revealed, *Chem. Eng. News.* **58** (30) 24 (1980); Berry, A Heavy, Sour Taste for Crude Oil Refiners, *Chem. Eng.* **87** (10) 96 (1980).
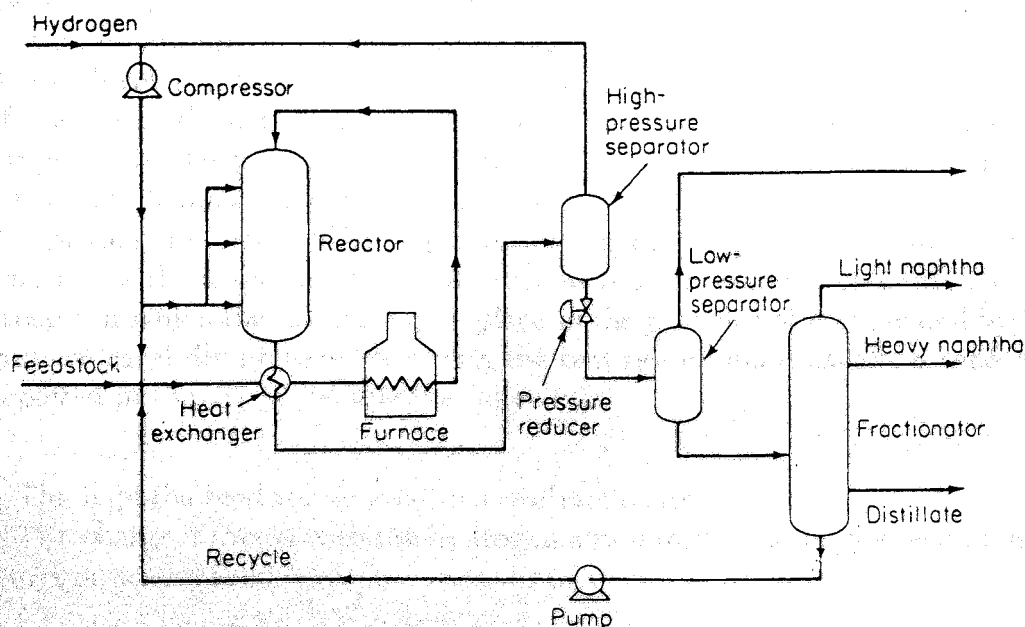

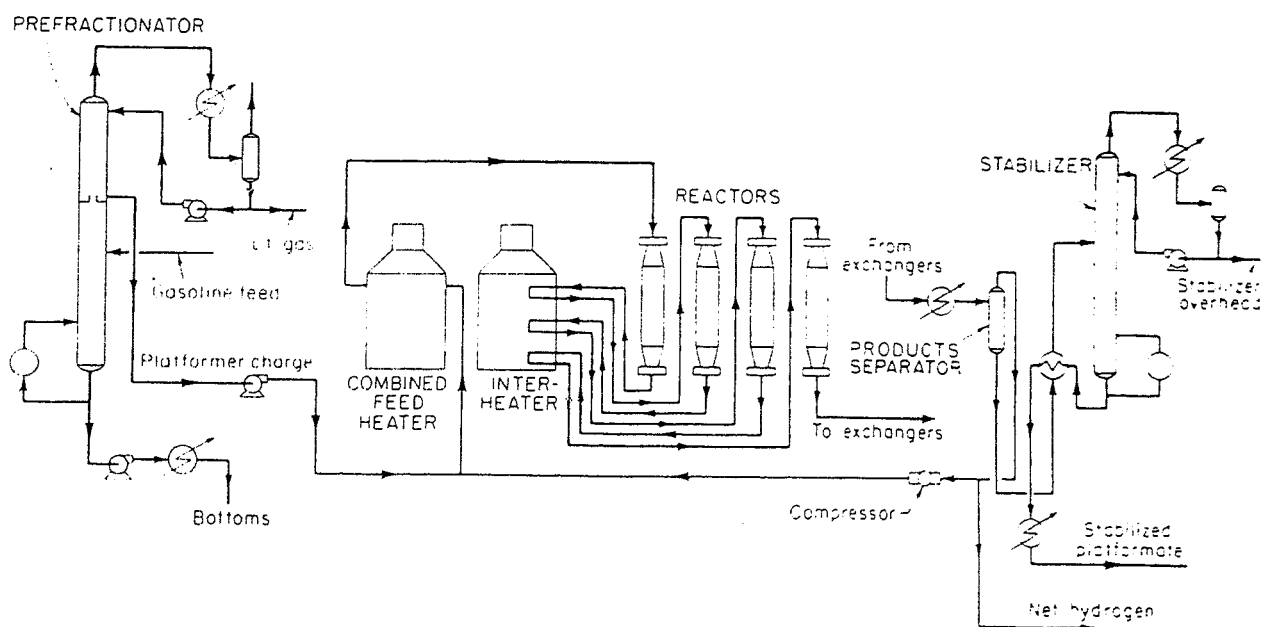Fig. 37.11 Hydrocracking.

PREFRACTIONATOR

Fig. 37.12. Flowchart for platforming. *(Universal Oil Products Co.)*

natural gasolines are low, these fractions are subjected to a high-temperature catalytic treatment, frequently in the presence of hydrogen, designed to preserve their present molecular size, but convert them into branched-chain and aromatic compounds with high antiknock ratings. This expensive process has become essential since the Environmental Protection Agency adopted the phase-out rules for lead. Without lead, enough high-octane motor fuel simply cannot be made without reforming—a combination of isomerization and cracking.

Catalytic Reforming. This involves the conversion of other hydrocarbons into aromatic compounds. Because of the high octane rating of aromatic compounds and the proved practicability of the process, catalytic reforming has now almost completely replaced thermal reforming. Catalysts such as platinum on alumina or silica-alumina and chromia on alumina are used. The Universal Oil Products Co. showed that these expensive catalysts could be used by reducing catalyst losses. Rhenium catalysts have come into use.

Another example of catalytic reforming is the *platforming* process[40] depicted in Fig. 37.12 It was developed by the Universal Oil Products Co. as an "economical commercial method of upgrading the octane ratings of straight run, natural and thermally cracked gasolines. and for producing large quantities of benzene, toluene, xylenes. and other aromatic hydrocarbons for use in chemical manufacture and in aviation fuel." The name comes from the fact that this process uses a fixed-bed Al_2O_3 catalyst containing 0.25% platinum. This catalyst has a long life without regeneration. The process is as an example of a specialized hydroforming process in which the reactions take place in the presence of recirculated hydrogen. The feed must be carefully prepared to obtain the best results and is usually a naphtha cut. The steps depicted in Fig. 37.12 include the following:

The naphtha feed is prepared in a prefractionator.

The charge is mixed with the hydrogen and introduced into the feed preheater, where the temperature is raised.

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[40]*Oil Gas J.* 70 (21) 52 (1972); Continuous Regenerator Smooths Naphtha Reforming, *Chem. Eng.* 79 (18) 80 (1972).

The hot-feed naphtha vapors are conducted with recycle hydrogen through the four cat-alyst-containing reactors in series with an interheating for each reactor. The temperature is 150 to 510°C and the pressure 1500 to 7000 kPa.

The reactions that take place are essentially as follows:

1. Isomerization of alkycyclopentanes to cyclohexanes.
2. Dehydrogenation of cyclohexanes to aromatics.
3. Dehydrocyclization of paraffins to aromatics.
4. Hydrocracking of paraffins and naphthenes.
5. Hydrogenation of olefins.
6. Isomerization of paraffins.
7. Desulfurization.

After the reactor, the products are cooled in heat interchangers. From the exchanger 90% hydrogen is obtained, compressed, and recycled. The main product is fractionated after the temperature is reduced to the proper point in heat exchangers and conducted into a fraction-ating column or stabilizer, the overhead from which may be used as fuel.

The product is stabilized *platformate*, which may be used as a high-octane gasoline or further fractionated into its constituents, e.g., to furnish benzene, toluene, and xylenes.

COKING. Lighter oils can be produced from very heavy ones by a solely thermal cracking process. The feed is usually a vacuum residue and considerable coke is formed. Delayed or fluid coking processes are used on low value residuals, avoiding catalyst fouling by asphalts which would otherwise make fluid catalytic cracking (FCC) difficult.

Another process known as Flexicoking takes the coke made and converts it into clean fuel gas by gasifying it with steam and air or oxygen.

Viscosity breaking is another thermal cracking process which is used to reduce the viscosity of heavy fuel oil.

Oxidation.[41] Oxidation-conversion as applied to petroleum gives more trouble than use-ful products, forming as it does gums and resins that interfere with the employment of gas-olines, particularly those which contain unsaturated compounds. However, some serviceable products are obtained from petroleum by oxidation, e.g., formaldehyde by restricted oxida-tion of methanol and by restricted oxidation of natural gas. Much study is also being directed toward making fatty acids[42] from paraffins and even food products. Blown asphalt is made by oxidation. Synthesis gas is made by partial oxidation of hydrocarbons,[43] and from it a wide variety of products are made including ammonia, methanol, and oxo-alcohols.

Polymerization.[44] Polymerization processes convert by-product hydrocarbon gases pro-duced in cracking into liquid hydrocarbons suitable for use as high-octane motor and aviation
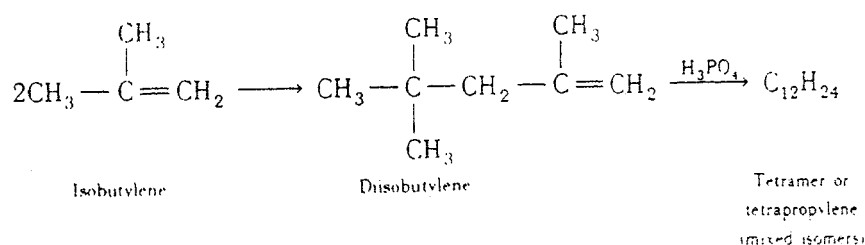
[41]Weismantel and Ricci, Partial Oxidation in Comeback, *Chem. Eng.* 86 (21) 57 (1974).

[42]Pardun and Kuchinka, Reaction Rates in the Liquid-Phase Oxidation of Paraffins, *Petrol. Refiner* 22 (11) 140 (1943); Partial Oxidation for Syngas and Fuel, *Hydrocarbon Process.* 53 (12) (1974).

[43]Marsh and Herbort, Synthesis Gas by Steam Reforming of Natural Gas, *Hydrocarbon Process.* 61 (6) 101 (1982); 61 (3) 92 (1982).

[44]Polygas Spells Relief from Alkylation Ills, *Chem. Eng.* 87 (12) 77 (1980).

fuels and for petrochemicals. To combine olefinic gases by polymerization to form heavier fractions, the combining fractions must be unsaturated. Hydrocarbon gases from cracking stills, particularly olefins, have been the major feedstock of polymerization. The following equation is typical of polymerization reactions. Propylene, normal butylene, and isobutylene are the olefins usually polymerized in the vapor phase.

$$2CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} = CH_2 \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \overset{\overset{CH_3}{|}}{C} = CH_2 \xrightarrow{H_3PO_4} C_{12}H_{24}$$

Isobutylene   Diisobutylene   Tetramer or tetrapropylene (mixed isomers)

Vapor-phase cracking produces considerable quantities of unsaturated gases suitable as feedstocks for polymerization units.

Catalytic polymerization is practical on both a large and a small scale and is adaptable to combination with reforming to increase the quality of the gasoline (Fig. 37.12). Gasoline produced by polymerization contains a smog-producing olefinic bond. Polymer oligomers are widely used to make detergents. Since the middle and late 1950s, polymerization has been supplemented by alkylation as a method of conversion of light C_3 and C_4 gases to gasoline fractions.

Alkylation.[45] Alkylation processes are exothermic and are fundamentally similar to polymerization; they differ in that only part of the charging stock need be unsaturated. As a result, the alkylate product contains no olefins and has a higher octane rating. These methods are based on the reactivity of the tertiary carbon of the isobutane with olefins, such as propylene, butylenes, and amylenes. The product *alkylate* is a mixture of saturated, stable isoparaffins distilling in the gasoline range, which becomes a most desirable component of many high-octane gasolines.

Alkylation is accomplished on a commercial scale with two catalysts: hydrogen fluoride and sulfuric acid. Alkylation with liquid hydrogen fluoride is illustrated by the flowchart in Fig 37.13. Here the acid can be used repeatedly, and there is no acid-disposal problem. The acid hydrocarbon ratio in the contactor is 2:1. The temperature range, from 15 to 35°C, is cheaply maintained, since no refrigeration is necessary. The simplified reaction is as given for the conversion process of alkylation, with a two- to threefold excess of isobutane over the butylenes to minimize realkylation of the primary alkylate. The anhydrous hydrofluoric acid, when dirty, is easily regenerated by distillation from heavy alkylate. Sufficient pressure is required on the system to keep the reactants in the liquid phase. Corrosion is low, and the separated isobutane is recycled. Also, alkylation results from the combination of an olefin or alkyl halide with an aromatic hydrocarbon (Chap. 38). The *Bergius process*, originated in Germany for the production of oils by hydrogenation of coal, finds no use in the United States at present. It has been tried in this country only on a semiworks scale. The synthesis of motor fuel from carbon monoxide and hydrogen is a hydrogenation process which was industrialized in Germany as the Fischer-Tropsch process[46] to make Synthol. The largest Fischer-

[45]Groggins, 5th ed., op. cit., p. 894 ff.

[46]Groggins, op. cit., p. 564; Kellogg, Synthol Process, *Petrol. Refiner*, November 1963, p. 42 (flowchart and description).
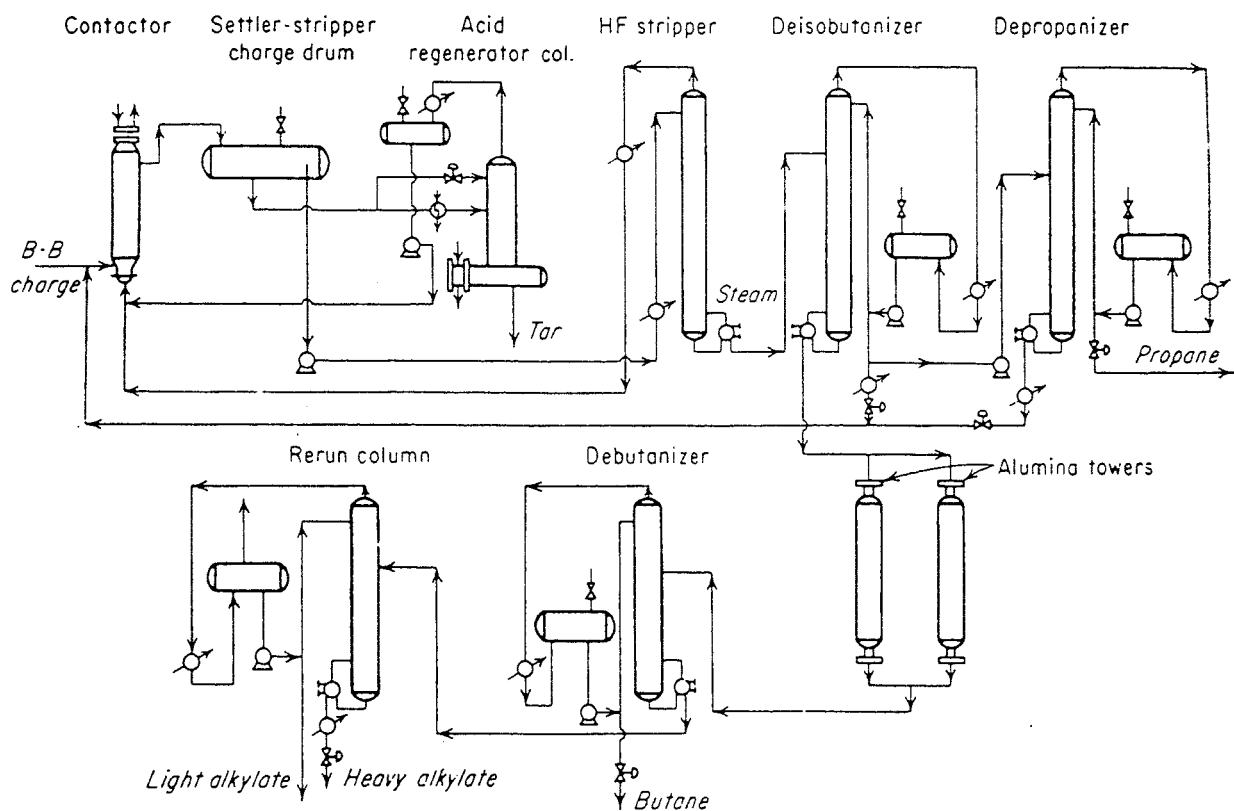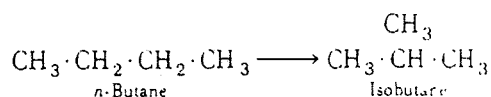
Fig. 37.13. Flowchart for HF alkylation. *(Universal Oil Products Co.)*

Tropsch plant is in South Africa, built by the M. W. Kellogg Co. This plant[47] has run successfully for over 25 years, producing motor fuels and other products for a petroleum-short country.

Isomerization.[48] This conversion process has become of the utmost importance in furnishing the isobutane needed for making alkylate as a basis for aviation gasoline (see alkylation). The reaction may be formulated:

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow CH_3 \cdot \overset{\displaystyle CH_3}{CH} \cdot CH_3$$
$$\text{n-Butane} \qquad\qquad \text{Isobutane}$$

CHEMICAL TREATMENT. Some type of chemical treatment to remove or alter the impurities in petroleum products is usually necessary to produce marketable material. Depending upon the particular treatment used, one or more of the following purposes are achieved:

1. Improvement of color.
2. Improvement of odor.
3. Removal of sulfur compounds.
4. Removal of gums, resins, and asphaltic materials.

[47]Dry, Sasol's Fischer-Tropsch Experience, *Hydrocarbon Process.* 61 (18) 121 (1982); Dry, The Sasol Route to fuels, *CHEMTECH* 12 (12) 744 (1982).

[48]Egloff, Hulla, and Komarewsky, *Isomerization of Pure Hydrocarbons*, Reinhold, New York, 1942; Liquid-Phase Isomerization, *Petrol. Refiner* 23 (2) 61 (1944).

5. Improvement of stability to light and air.
6. Improved susceptibility to additives.

Of these, removal of sulfur[49] and improvement of stability are the factors usually governing the treatment employed. With the discovery that the use of catalytic converters causes the emission of sulfuric acid vapors from automobile exhausts, pressure to remove or reduce sulfur in motor fuel has developed. Sulfur may be reduced by (1) hydrogenation (which also removes metals and nitrogen), (2) treatment with caustic soda, (3) treatment with caustic soda plus a catalyst (Merox), and (4) treatment with ethanolamines.

Several processes are available for the alteration of objectionable sulfur and the consequent improvement in odor. The *doctor treatment* was the original method of "doctoring" the oil to reduce the odor and utilized sodium plumbite to convert mercaptans to less objectionable disulfides. A number of processes are now aimed at removing sulfur-containing compounds. Hydrogen treatment reduces the sulfur in heavy fractions and resids. Hydrogen or hydrogen-donor liquids and a catalyst are used to treat lighter distillates, removing nitrogen, sulfur, and some metallic contaminants as well. Extraction with caustic or proprietary solutions (usually oxygen-regenerable) is frequently used on light distillates.

It is now common practice to add antioxidants to prevent the formation of gums, rather than to remove them chemically. Among the *antigumming* materials used are α-naphthol, substituted catechols, cresols, benzyl-*p*-aminophenols, and certain wood-tar and coal-tar fractions.

WASTE TREATMENT. Sulfur compounds in stack gases and a variety of extracts and wastes found in refinery waste waters must be disposed of. Treatment of these two types of wastes to give acceptable environmental control now approaches the size and cost of the remainder of the refinery.

Research. The petroleum industry has been characterized by continuous improvement based upon research and a willingness to replace antiquated equipment or old processes by more modern ones. This development went through two phases. In the first phase, the *unit operations*, distillation, heat transfer, fluid flow, and the like, were subjected to accurate study and experimentation; these operations could be carried out with greater efficiency and consequently less cost. However, the second phase of research was the study of chemical changes involving petroleum raw materials and petroleum products.

Most current research seeks new and better catalysts, or improvements in old processes. Little basic research is being done. Very expensive developmental research continues to be done on other sources of oil supply. Shale oil mining and retorting, oil sands recovery procedures, coal liquefaction, biomass conversion to fuel, and gasohol from grain are examples of fields being actively studied now.

To maintain a competitive and well-rounded position many petroleum compounds must be chemically altered to obtain products of greater usefulness or value. Each year shows a higher percentage of petroleum sales from the action of chemical change on petroleum raw materials. Indeed, the petroleum industry has become the most important source of cheap raw materials for the entire chemical industry. Such chemical change will be more marked in the future than it has been in the past. The present sound technical position has come about as a result of technical research protected by patents, but proportionately less money is being spent on research than in the past.

[49]A Sulfur in Gasoline Scare? *Chem. Eng.*, 81 (26), 74 (1974); Ranney, *Desulfurization of Petroleum*, Noyes, Park Ridge, N.J., 1975.

Other Products from Petroleum. Because petroleum contains so many constituents and is reactive in so many different ways, new products are constantly being sought and found. After conversion to methanol, it is possible to grow single-cell protein suitable for human and animal food. Bacteria can also grow on methane and other hydrocarbons.[50] Several large plants have been built in Europe and Asia, but acceptance of the products has been disappointing.

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[50]Skinner, Single Cell Protein Moves toward Market, *Chem. Eng. News* 53 (18) 24 (1974); Harrison, Making Protein from Methane, *CHEMTECH* 6 (9) 570 (1976).